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THIN STRIPS OR FOILS MADE OF AlFeSi ALLOY

Domain of the invention

This invention concerns thin strips or foils less than 200 µm thick and preferably less than 50 µm thick, made of an aluminium alloy with iron and with silicon, with substantially low manganese content, and a process of manufacturing such strips or foils. These strips may be obtained by semi-continuous casting of conventional plates or by continuous casting, for example by twin-belt casting or twin-roll casting.

State of the art

The trend in the thin aluminium alloy foil market is moving towards a constant reduction in the thicknesses used for a given application, while demanding high mechanical properties and good formability.

Alloys with a very low manganese content are frequently used for thin foil, for example such as the 8111 alloy with the following composition (% by weight) registered with the Aluminum Association:

Si 0.30 – 1.1; Fe 0.40 – 1.0; Cu < 0.10; Mn < 0.10

The lack of manganese makes it easy to obtain recrystallisation during the final annealing, but the ultimate tensile strength R_m remains insufficient for thicknesses less than 100 µm.

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Therefore, there is a need to develop new alloys and / or to optimise transformation procedures to satisfy market demand.

Manganese is normally added to increase the mechanical strength, for example as in the 8006 alloy for which the composition (% by weight) registered with the Aluminum Association is as follows:

Si < 0.40; Fe : 1.2 – 2.0; Cu < 0.30; Mn : 0.30 – 1.0; Mg < 0.10

The result of adding manganese is to harden the material. The mechanical properties obtained with patent US 6 517 646 belonging to the applicant for an alloy with composition Si = 0.23%; Fe = 1.26%; Cu = 0.017%; Mn = 0.37%; Mg = 0.0032%; Ti = 0.008%, in combination with a favourable transformation procedure, gives a value R_m equal to 103 MPa for a thickness of 6.6 μm.

The mechanical properties can also be improved by adding a small quantity of manganese in alloys in the 8000 series containing iron. Patent application WO 02/64848 (Alcan International) describes the fabrication of thin strips made of AlFeSi alloy containing from 1.2% to 1.7% Fe and 0.35% to 0.8% of Si, by continuous casting. A high mechanical strength is obtained by adding 0.07% to 0.20% of manganese to the alloy. This addition of manganese is recognised as being necessary to obtain a small grain size after final annealing.

Therefore, manganese appears to be an element capable of improving the mechanical properties of 8000 alloys. However, manganese in solid solution or in the form of fine precipitates can block or delay recrystallisation during final annealing. Therefore, the precipitation of phases containing manganese needs to be controlled precisely during each step in the procedure, which is often difficult. Any drift in the transformation procedure has non-negligible consequences on the effectiveness of the final annealing. Therefore, it would be very useful to develop an alloy that does not contain any manganese, but that does have high mechanical properties.

US Patent 5 503 689 (Reynolds Metals) describes a process for manufacturing a thin strip made of an alloy containing 0.30% to 1.1% Si and 0.40% to 1.0% Fe, less than 0.25% Cu and less than 0.1% Mn, by continuous casting and cold rolling without

intermediate annealing. The preferred contents of iron and silicon are between 0.6% and 0.75%.

US Patent 5 725 695 (Reynolds Metals) describes a procedure for the same composition, with intermediate annealing between 400°C and 440°C (750°F – 825°F) and a final recrystallisation annealing at 288°C (550°F). The ratio of the Si and Fe contents is greater than or equal to 1. In the examples, the maximum ultimate tensile strength obtained is 90 MPa (13.13 ksi), the maximum yield stress is 39.1 MPa (5.68 ksi), and the elongation is 11.37% for thicknesses of 46 μm (0.00185'). These mechanical properties are still low for some applications.

For alloys obtained by continuous casting, it is often necessary to perform a high temperature heat treatment to reduce the noxiousness of segregations, by resorbing precipitation lumps and homogenising the structure through the thickness. The effect of a homogenisation at 600°C for the 8011 alloy (composition 0.71% Fe; 0.77% Si; 0.038% Cu; 0.006% Mn; 98.45% Al) obtained by twin-roll casting is described in the article by Y. Birol "Centerline Segregation in a Twin-Roll Cast AA8011 Alloy", Aluminium, 74, 1998, pp 318 – 321. The precipitated phases are modified and heterogeneities are reduced. The reduction in central segregation subsequently limits the porosity of very thin foils and improves their formability.

It is economically attractive to limit the heat treatment temperature. For an 8111 alloy with composition 0.7% Fe; 0.7% Si; Mn < 0.02, Zn < 0.02; Cu < 0.02, a beginning of a transformation of the phases is observed with total recrystallisation at 460°C, although annealing at 550°C – 580°C is necessary to obtain a more complete transformation (see M. Slamova et al. "Response of AA8006 and AA8111 Strip-Cast Rolled Alloys to High Temperature Annealing", ICAA-6, 1998). Therefore low temperature homogenisation could be considered for alloys without manganese.

Moreover, in the transformation to low thicknesses subsequent to homogenisation, it is standard practice to add an intermediate annealing step in order to soften the metal. For manganese alloys, the intermediate annealing control usually

requires a high temperature heat treatment (at above 400°C) so as to obtain recrystallisation.

For manganese-free 8000 type alloys, it is possible to envisage a heat treatment at a lower temperature than for 8006 type alloys.

Patent application WO 99/23269 (Nippon Light Metal and Alcan International) describes a process applicable to AlFeSi alloys containing 0.2% to 1% of Si and 0.3% to 1.2% of Fe, with a Si/Fe ratio of between 0.4 and 1.2, in which intermediate annealing is done in two steps, the first between 350°C and 450°C, and the second between 200°C and 330°C. The purpose of this process is to reduce surface defects in the foil. Mechanical properties are not mentioned.

The purpose of the invention is to obtain thin strips or foils made of an AlFeSi alloy with no added manganese, with a high mechanical strength while maintaining good formability, with the most economic industrial manufacturing procedure possible.

Subject matter of the invention

The subject matter of the invention is a thin foil between 6 µm and 200 µm thick, and preferably between 6 µm and 50 µm thick, of an alloy with the following composition (% by weight):

Si :1.0 – 1.5; Fe : 1.0 – 1.5; Cu < 0.2; Mn < 0.1; other elements < 0.05 each and < 0.15 total, remainder Al, preferably with the condition Si/Fe $\geq$ 0.95, with an ultimate tensile strength in the annealed temper R_m > 110 MPa for thicknesses > 9 µm and > 100 MPa for thicknesses between 6 µm and 9 µm. The yield stress $R_{0.2}$ of the thin foil (measured on sheared test pieces) is preferably > 70 MPa. The ultimate elongation is greater than the following values, as a function of the thickness of the foil:

Thickness (µm)	A (%) greater than	and preferably than
6 – 9	3	4
9 – 15	5	7
15 – 25	10	15

25 – 50	18	25
50 – 200	20	25

The silicon content of the alloy is preferably between 1.1% and 1.3% and its iron content is between 1.0% and 1.2%.

Another subject matter of the invention is a manufacturing process for thin strips thinner than 200 µm made of an Al-Fe-Si alloy with composition (% by weight): Si : 1.0 – 1.5; Fe : 1.0 – 1.5; Cu < 0.2; Mn < 0.1; other elements < 0.05 each and < 0.15 total, remainder Al, preferably with the condition Si/Fe ≥ 0.95, including the preparation of a first strip either by vertical semi-continuous casting of a plate and hot rolling, or by continuous casting possibly followed by hot rolling, cold rolling of this first strip down to the final thickness, possibly with intermediate annealing for between 2 h and 20 h at a temperature between 250°C and 350°C, and preferably between 280°C and 340°C, and final annealing at a temperature between 200°C and 370°C.

Description of the invention

The thin strips or foils according to the invention are made from 8000 AlSiFe alloys with almost no manganese, typically less than 0.1%. Iron and silicon contents are significantly higher than 8011 and 8111 alloys that are the most frequently used manganese-free AlSiFe alloys for thin foil. One preferred composition range is an alloy containing 1.1% to 1.3% of silicon and 1.0% to 1.2% of iron.

Alloys according to the invention preferably have a composition such that the Si/Fe ratio of silicon and iron contents is ≥ 0.95. Their mechanical strength in the annealed temper (O temper) is exceptional for alloys with this composition, with an ultimate tensile strength R_m > 110 MPa or even 115 MPa for thicknesses > 9 µm, and > 100 MPa for thicknesses from 6 µm to 9 µm, and a conventional yield stress at 0.2%, $R_{0.2}$ > 70 MPa. This high mechanical strength is not obtained at the expense of formability, since elongations are at least as high as for 8011 and 8111 alloys, and bursting pressures are higher.

These high mechanical properties are obtained equally well for strips produced from plates obtained by conventional vertical semi-continuous casting and hot rolled, and for strips derived from continuous casting, either by belt casting or twin-roll casting. Continuous belt casting is also following by hot rolling.

Hot rolled strips, or as-cast strips obtained by continuous twin-roll casting, may be homogenised at low temperature (between 450°C and 500°C) to reduce the central segregation that may reduce formability to the final thickness. This low temperature heat treatment is sufficient to resorb any central segregations in these manganese-free alloys. The strips are then cold rolled, either down to the final thickness or to an intermediate thickness between 0.5 mm and 5 mm, at which an intermediate annealing is performed. Unlike alloys containing manganese, this intermediate annealing can be done at a relatively low temperature between 250°C and 350°C, and preferably between 280°C and 340°C, for longer than 2 hours. Although this temperature range is described in the literature, particularly in patent application WO 02/064848 mentioned above, it is below the normal range that remains above 400°C.

The applicant has observed that the application of low temperature heat treatments to an AlFeSi alloy, more particularly with a composition such that Si/Fe > 0.95, possibly eliminating the intermediate annealing when technically possible, results in significantly higher mechanical strength than is possible with normal intermediate annealing, at least 15% better. This higher mechanical strength is obtained while improving the formability measured by the bursting pressure or the dome height according to standard ISO 2758.

Final annealing is done at a temperature between 200°C and 370°C for between 1 h and 72 h. Annealing durations depend on the degreasing quality of the foil. A fine grain structure is obtained after annealing, with an average grain size measured by image analysis with a scanning electron microscope equal to less than 3 μm.

The combination of low temperature homogenisation or no homogenisation at all with an intermediate annealing at low temperature or no intermediate annealing at all, is economically advantageous but also helps to obtain a fine grain size. The grain size is

about 30% lower than is possible with heat treatments at a higher temperature, consequently increasing the mechanical properties $R_{0.2}$ and R_m which for small thicknesses are related to the number of grain joints. This gain is not achieved at the detriment of elongation, since the increase in the number of grains in the thickness also limits the risk of local damage in one or two single grains in the thickness of the foil.

Thin foils according to the invention are particularly suitable for applications requiring good mechanical strength and high formability, for example such as fabrication of multi-layer composites, particularly for lids for packaging of fresh products, overcaps or aluminium wrapping.

Examples

Example 1

Two 6.1 mm thick strips made of alloy A according to the invention and alloy B type 8111 with the composition (% by weight) indicated in table 1 were made by continuous twin-roll casting, in order to demonstrate the influence of the composition of the alloy:

Table 1

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Ti	B
A	1.17	1.11	0.001	0.003	0.0004	0.0007	0.006	0.0005
B	0.7	0.7	0.001	0.003	0.0005	0.001	0.007	0.0005

The strips were cold rolled to a thickness of 2 mm and an intermediate annealing was then carried out on them for 5 hours at 320°C. The strips were then cold rolled in several passes to the final thickness of 38 µm. A final annealing was then carried out on them for 40 hours at 270°C.

The mechanical properties were measured in each case. The measured values were the ultimate tensile strength R_m (in MPa), the conventional yield stress at 0.2% $R_{0.2}$ and the ultimate elongation A (in %) according to standard NF-EN 546-2, the bursting

pressure in air Pe (in kPa) measured according to standard ISO 2758 and the dome height Hd (in mm). The results are given in table 2:

Table 2

Alloy	R_m (MPa)	$R_{0.2}$ (MPa)	A (%)	Pe (kPA)	Hd
A	123	76	30	394	9.2
B	104	54	15.8	284	6.6

It is found that, unlike the 8111 type alloy B, the ultimate strength of the alloy A strip is much higher than 110 MPa, and the yield stress is higher than 70 MPa. The bursting pressure and the elongation are also higher, such that this alloy is both stronger and more formable.

<u>Example 2</u>

A 6.1 mm thick strip made of alloy A described in example 1 was made by continuous twin-roll casting. The strip was then cold rolled to a thickness of 2 mm. A normal intermediate annealing for an alloy of this type was then carried out on part of the strip, for 5 hours at 500°C. An intermediate annealing was carried out on the other part of the strip, for 5 hours at 320°C according to the invention. The two parts of the strip were then cold rolled in several passes to the final thickness of 10.5 µm. A final annealing was then carried out on them for 40 hours at 270°C.

The properties were the same as in example 1, and the values are shown in table 3:

Table 3

Inter. annealing	R_m (MPa)	$R_{0.2}$ (MPa)	A (%)	Pe (kPa)	Hd (mm)
470°C	99	63	7.3	71	5.1
320°C	117	84	8.1	92	5.7

It is found that the lower temperature of the intermediate annealing increases the mechanical strength, the elongation, the bursting strength and the formability.

The average grain size measured by image analysis with an SEM, is 3.6 μm for annealing at 470°C, and 2.3 μm for annealing at 320°C. Therefore the increase in mechanical properties for low temperature annealing is related to the reduction in grain size obtained after final annealing.